FEBRUARY 24, 2020

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R&D OF UHTR &UHTR FIBER-REINFORCED COMPOSITES

NASA AMES RESEARCH CENTER
MOFFETT FIELD, CA

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#UT Austin/KAI, LLC, Austin, TX

TECHNEGLAS
UHTR Resin Technology

Outline

- Overview of Techneglas Products
- Ablation R&D Capabilities of Koo Research Group
- Study Case 1: Char Yield Studies
- Study Case 2: Experimental Characterization of Material Properties of Novel Silica/Polysiloxane Ablative
- Overall Concluding Remarks & Ongoing Projects/Plans
- Acknowledgements
- Study Case 3: Vertical Launching (VLS) MK 41 Study*

*ITAR

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OVERVIEW OF TECHNEGLAS PRODUCTS

Techneglas Intro

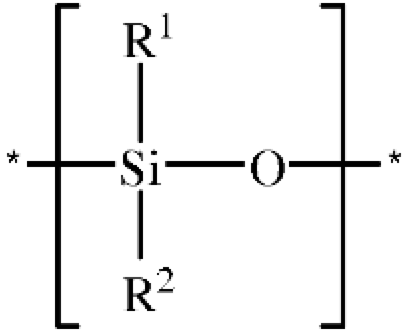
TECHNEGLAS
UHTR Resin Technology

- Techneglas was the Technical Products Division for Owens-Illinois (OI) from ~1946-1988
- Techneglas (OI) developed resins for high temperature mold release
- Techneglas (OI) developed competencies related to cathode-ray tube (CRT) manufacturing
- OI had technology assistance agreement for color TV technology 1960's – 80's
- Techneglas manufactures Glass Resin polysiloxane polymers for a variety of applications:
    - Abrasion resistant coatings for plastics
    - Electronics coatings
    - Mold release agents
    - High temperature applications

UHTR Resin Introduction

TECHNEGLAS
UHTR Resin Technology

- UHTR composite resin is
  - Formulated for composite parts requiring service temperatures above 500°F (260°C), up to 1800°F (980°C)
  - Inorganic polysiloxane matrix
  - Pre-ceramic material
  - Patented technology (US 10,259,972, US 10,538,685)
- UHTR exhibit
  - Low weight loss / high char yield
  - Low heat release rate
  - Low heat release capacity
- UHTR is formulated for composites using standard reinforcements
- Currently working to develop UHTR pre-preg



UHTR Resin Variations

Liquid

- UHTR-IPA — 65% resin solids in Isopropyl Alcohol, 100 cps @25°C

Solid Flake (F)

- UHTR-F — Solid Flake resin, m.p. 100°C

Solventless (S)

- UHTR M63-S — Liquid resin, 1200 cps @25°C
- UHTR 6398-S — Liquid resin, 15,000 cps @75°C

UHTR Product Applications

TECHNEGLAS
UHTR Resin Technology

Currently specializes in *"Polymer Nanocomposites Technology Designed for Extreme Environments" funded by DoD, DoE, DoT, NASA, and private companies:*

Ablation Research:

- *Solid rocket motor (SRM) nozzle ablatives using polymer nanocomposites*
- *Rocket nozzle erosion minimization (RNEM)*
- *Experimental and numerical characterization of SRM internal insulation materials*
- *Functionally graded polyetherimide nanocomposite foams for space application*
- *Missile/propulsion/re-entry thermal protection systems (TPS) ablatives characterization*
- *In-situ ablation and thermal sensors for TPS and SRM ablatives*
- *Char strength sensors to evaluate polymer nanocomposite ablatives*
- *Ablative, thermal, and flammability properties of SiC fiber-reinforced ceramic matrix composites*
- *Material response (MR) modeling to evaluate ablation recession and thermal characteristics*
- *Re-design oxy-acetylene test bed with advanced diagnostics*
- *Innovative nanostructured ablatives for re-entry missile structures*
- *Thermophysical properties characterization of high-temperature resins and their fiber-reinforced composites*
- *Ablative, thermal, and flammability properties of 2D silica/polysiloxane composites*
- *Affordable elastomeric insulation material for SRMs with improved ablation resistance*
- *2.5D silica woven fiber-reinforced/polysiloxane composites for aerospace applications*
- *Materials for 3D printed heat shield*
- *CFD flowfield coupled with material response modeling of ablative systems*
- *Affordable polymer nanocomposite ablatives for MK 41 Vertical Launching Systems (VLS)*
- *Ultra-performance polymers for 3D printed heat shield*
- *Aerothermal ablation testing with insitu ablation sensor/material response ablation modeling of glass/phenolic ablatives*
- *High-temperature materials testing and development for hypersonics*
- *Novel additively-manufactured composite external hypersonic heat shield*
- *Dual layer polysiloxane fiber-reinforced composite: Top recession layer (RL) of carbon/polysiloxane MC and bottom insulating layer (IL) of glass mat/polysiloxane composite*
- *3D printed dual layer neat PEKK polymer: Top RL of 100% infilled and bottom IL of 75% and 50% infilled lattice structures*
- *Polysiloxane/aerogel short fiber-reinforced composite for better insulation*
- *Carbon fiber surface treatment compatible with polysiloxane to enhance interfacial bonding (with RMIT University, Melbourne, AU)*

Flame Retardant Polymers Research:

- *Flame retardant polymers for selective laser sintering (SLS), fused deposition modeling (FDM), & Jet Fusion 3D (JF3D) in additive manufacturing (AM)*
- *Flame resistant fabrics/textiles via electro-spinning/melt-spinning*
- *Numerical modeling of polymer degradation kinetic parameters*

Conductive Polymers Research:

- *Electrically and thermally conductive polymers for SLS, FDM, & JF3D in AM*
- *Multifunctional cyanate ester-f-CNT nanocomposites carbon fiber-reinforced composites*
- *High thermally conductive epoxy graphite fiber-reinforced composites*
- *Scale-up highly aligned and high concentration CNT-reinforced composites for aerospace applications*
- *Hybrid ceramic matrix composite/polymer matrix composite (CMD-PMC) skin materials*

Others: *Nanomodified carbon/carbon composites; High and low temperature resins and their glass reinforced filament wound composites for downhole drilling; Welding of high-performance bridge steel; Monitoring technology for nuclear explosions high reliability whole-air compressor.*

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ABLATION R&D CAPABILITIES OF KOO RESEARCH GROUP

Koo Research Group (KRG) R&D

- KRG specializes in R&D of novel polymer nanocomposites that can be used in extreme environments through processing, fabrication, and characterization.
- Processing: use Design of experiments (DOE) to develop a composite matrix to be compounded.
- Characterization (step A): characterize composite formulations to down select for model fabrication.
- Fabrication: produce test specimens using techniques, such as compression molding and 3D printing for material properties characterization.
- Characterization (step B): characterize material ablation properties of the fabricated test models using oxy-acetylene test bed (OTB) and inductively coupled plasma (ICP).

Materials Property Characterization Capabilities

- Physical: Density
- Thermal: TGA, DSC, MFI, Laser Flash
- Morphological: SEM, TEM
- Flammability: MCC, UL 94, LOI, HDT, Cone Calorimetry
- Ablation: OTB, ICP
- Electrical: ESD
- Mechanical: Tensile, flexural, Izod impact

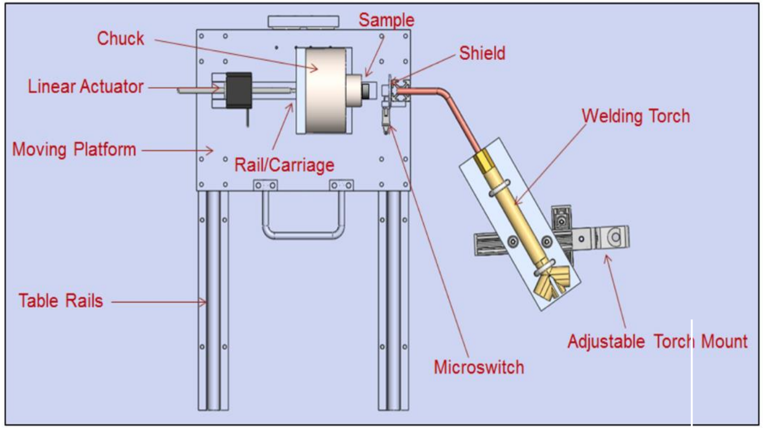
OTB testing

Purpose

Characterize: Mass loss, Recession, Surface temperature, In-depth temperature, Backside temperature, and Surface behavior during aerothermal testing

Parameters

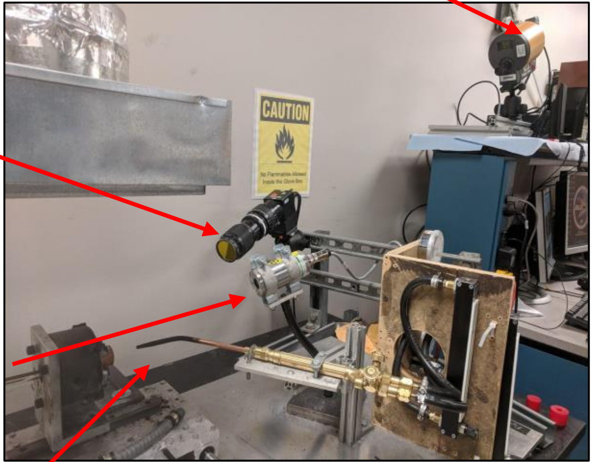
Heat flux 100 – 1,600 W/cm^2



OTB Test Setup Diagram

IR Camera

HD Camera

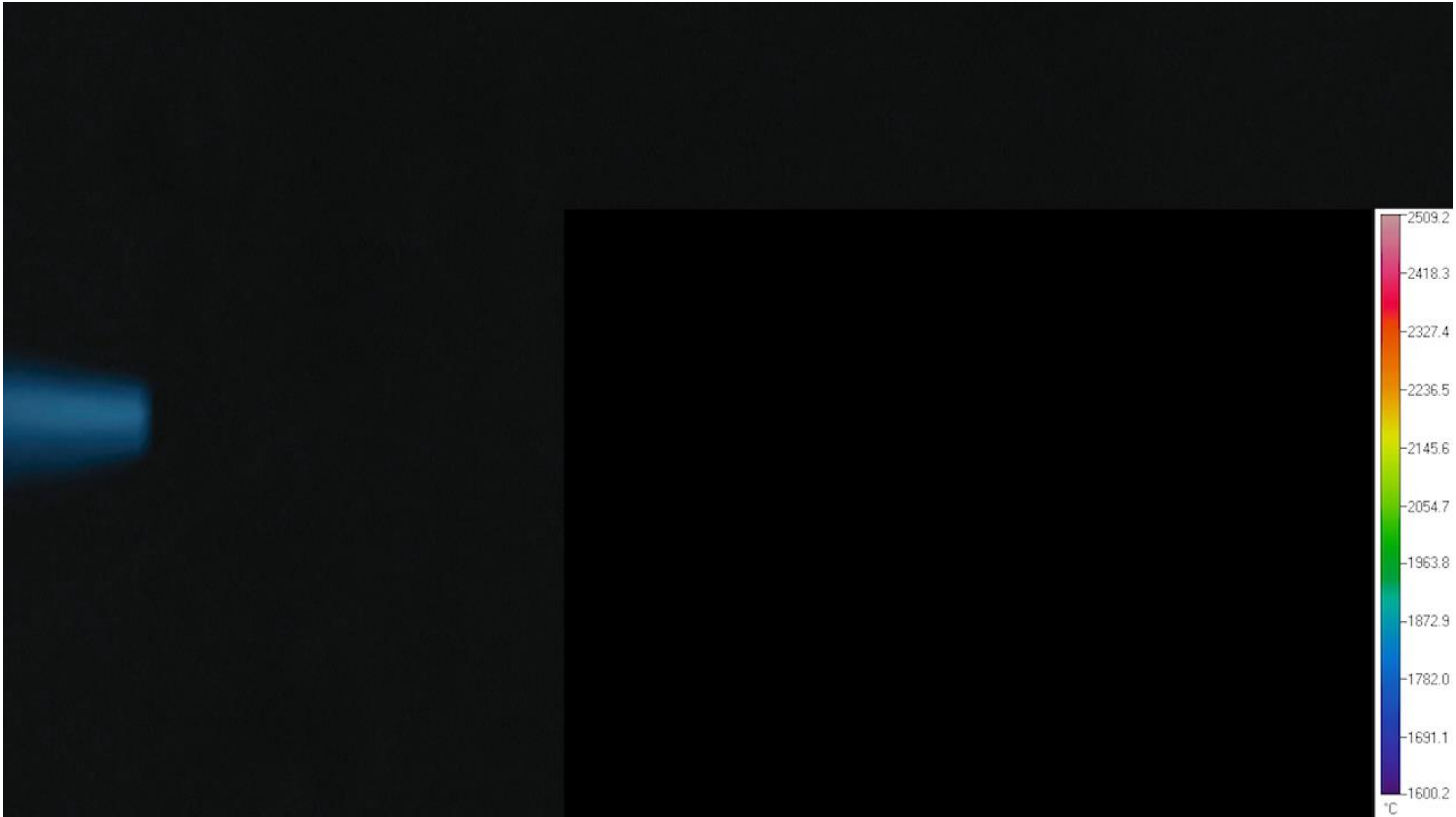


IR Pyrometer

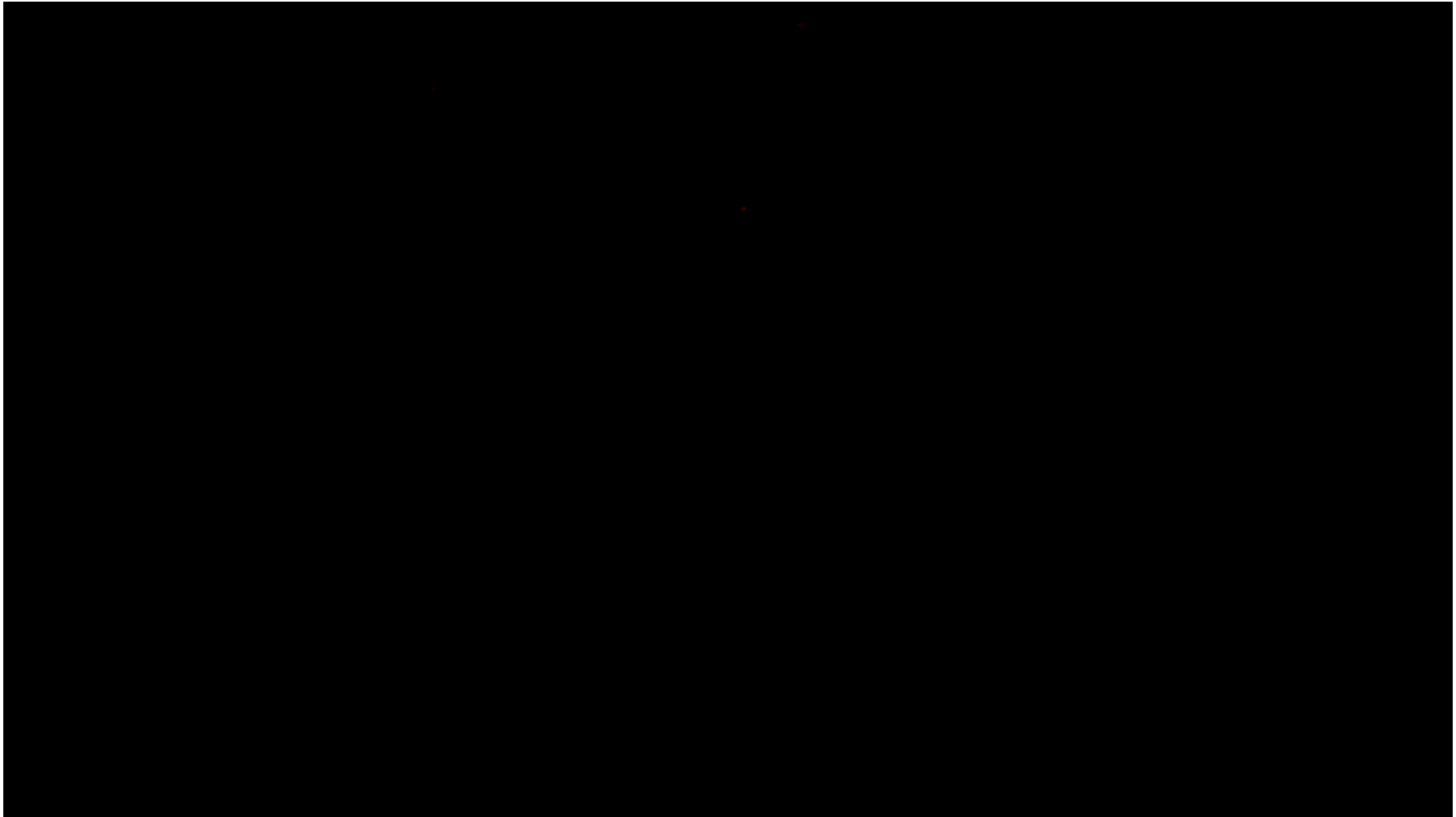
Oxyacetylene Flame

OTB Test Setup

MXB-360 at 1,000 W/cm^2 for 60 s



3D Printed PEKK at 100 W/cm^2 for 30 s



Case Study 1: Char Yield, Thermal Stability, & Kinetic Parameters*

*Funded by KAI, LLC

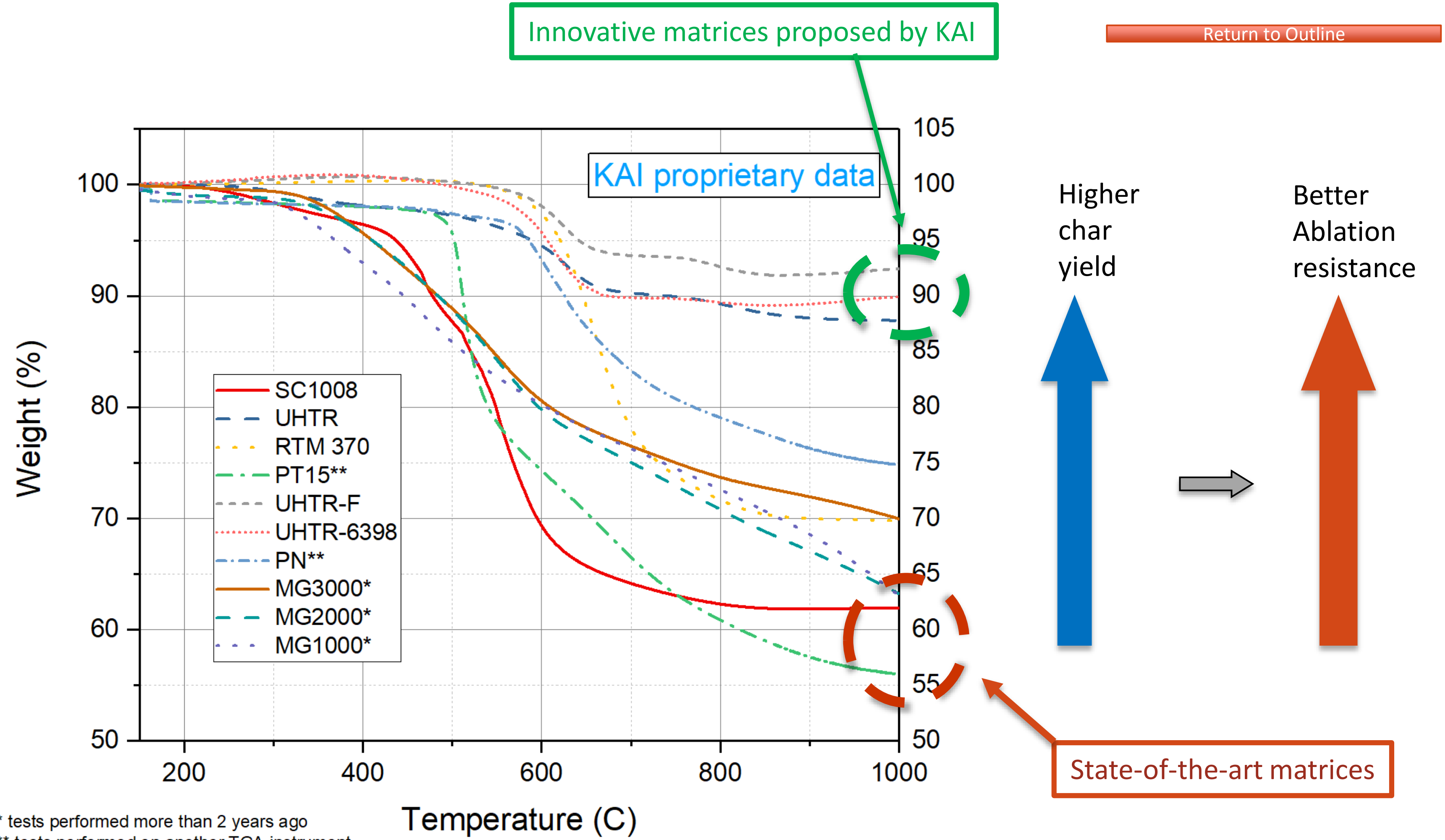
Char Yield Definition*

1. Dry the TGA test specimens at 150°C for 30 min
2. Consistent sample size – 20 mg
3. TGA heating rate of 20°C/min in nitrogen
4. Char yield is defined as the %mass remaining at 1,000°C

*Adopted from a NASA report on PICA

Char Yield - Materials Investigated

- **SC-1008** – Legacy phenolic resin
- **PT-15** – Cyanate ester resin
- **PN** – U.S. Naval Research Laboratory (NRL) developed PEEK-like phthalonitrile (PN) resin
- **UHTR (DT1116-1), UHTR-F, UHTR-6398** – Polysiloxane resin
- **MG Resins** – MG1000, MG2000, MG2000C, and MG3000
- **NASA-GRC** – RTM370 polyimide (PI) resin
- **Others** – PBI, Starfire, nano-modified SC-1008



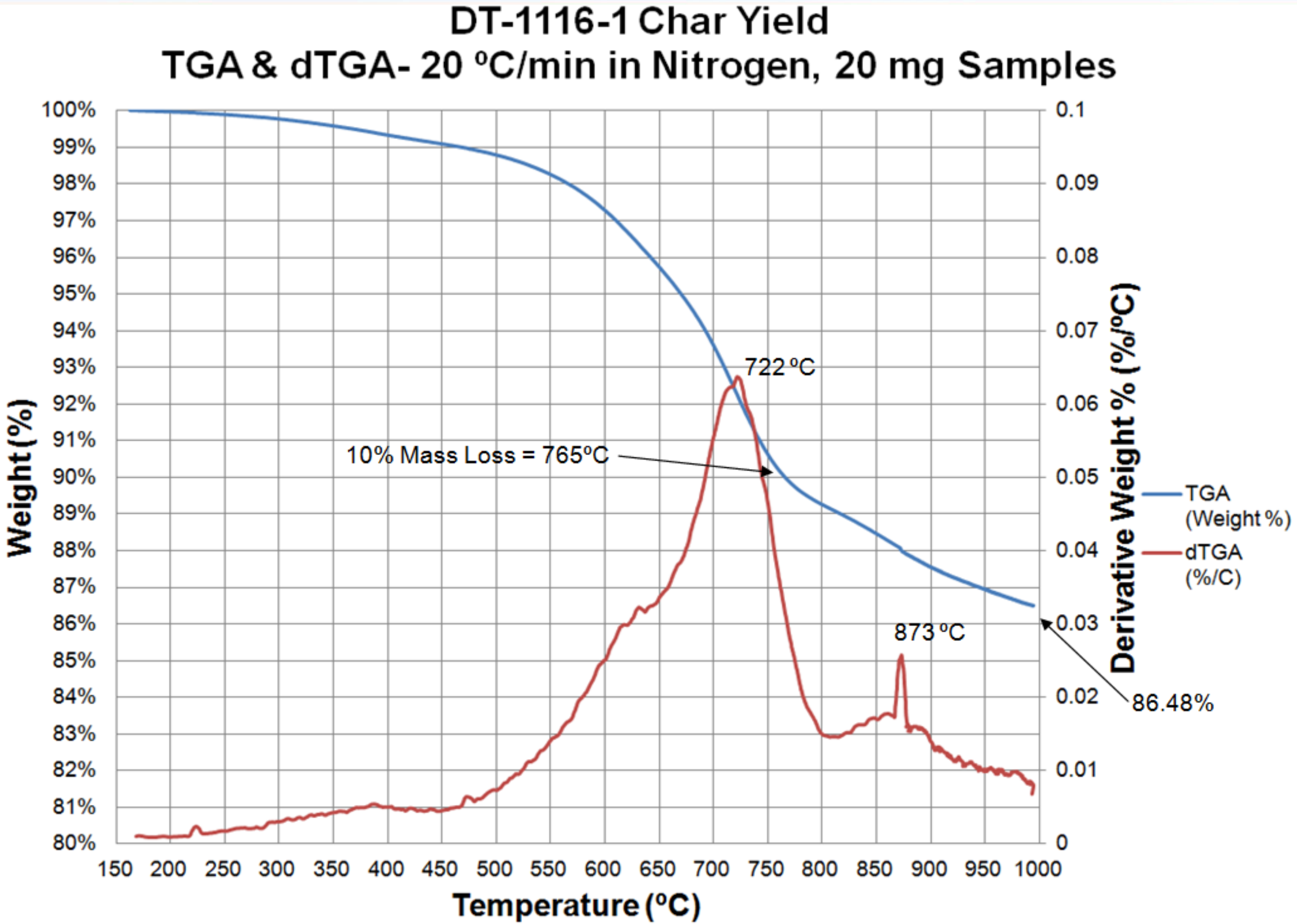
* tests performed more than 2 years ago
** tests performed on another TGA instrument

Decomposition Temperature (T_d) & Char Yield

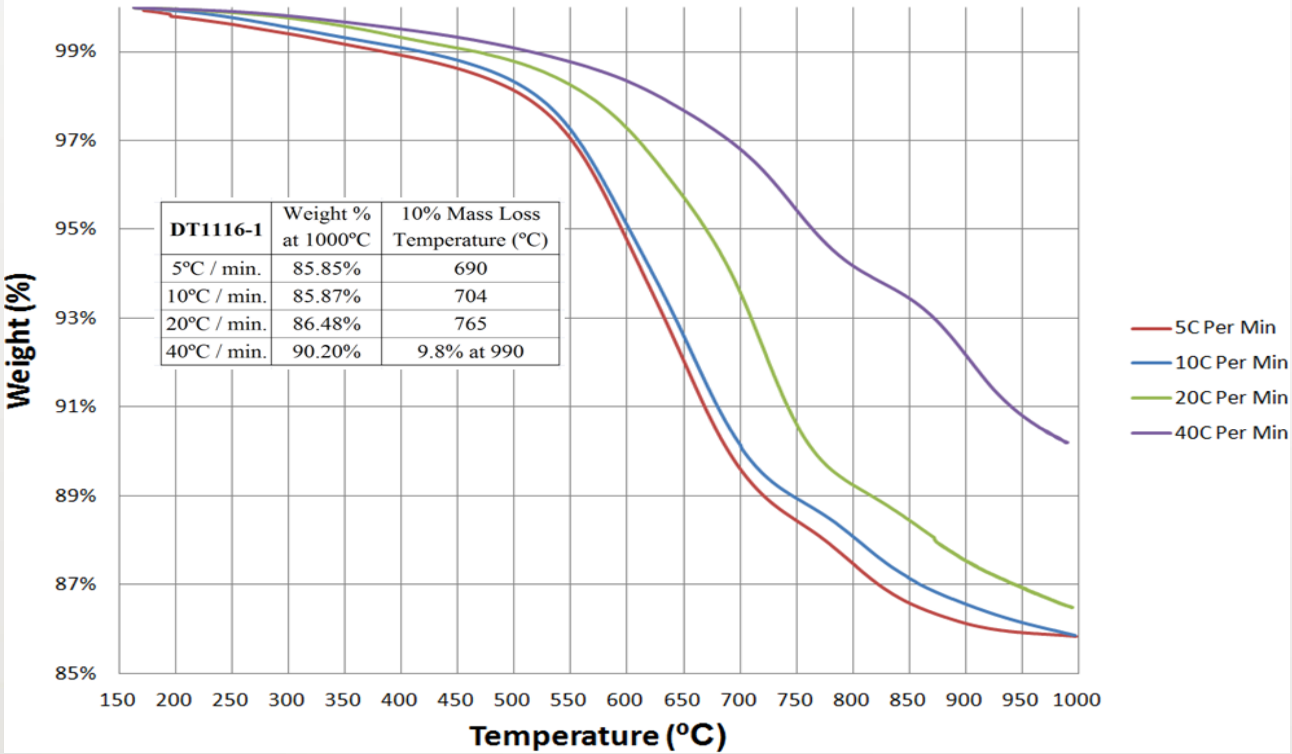
Material	T_d @ 10% (^oC)	Char yield (%)
UHTR-F	-	92.4
UHTR-6398	673	89.9
UHTR	765	86.5
PN	636	74.8
MG3000	484	70.0
RTM 370 (PI)	646	69.8
MG2000	484	63.2
MG1000	446	63.1
PT15	511	56.9
SC1008	468	56.2

Thermal Stability & Kinetic Parameters of Thermal Decomposition Reactions

- **Four Heating Rates** – 5, 10, 20, and 40ºC/min from 163ºC to 1,000ºC in nitrogen
- **dTGA Studies** to identify the no. of reactions
- **Isoconversion Code** was used to calculate the kinetic parameters
- **Materials** – Neat resin (SC-1008, PT-15, PN, UHTR, & others)


DT-1116-1 Char Yield
TGA & dTGA- 20 ºC/min in Nitrogen, 20 mg Samples
Weight (%)
100%
99%
98%
97%
96%
95%
94%
93%
92%
91%
90%
89%
88%
87%
86%
85%
84%
83%
82%
81%
80%
Derivative Weight % (%/ºC)
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
Temperature (ºC)
722 ºC
10% Mass Loss = 765ºC
873 ºC
86.48%
TGA (Weight %)
dTGA (%/C)

UHTR (DT1116-1) Thermal Stability, T_d, and Residual Mass



DT1116-1	Weight % at 1000°C	10% Mass Loss Temperature (°C)
5°C / min.	85.85%	690
10°C / min.	85.87%	704
20°C / min.	86.48%	765
40°C / min.	90.20%	9.8% at 990

Summary & Concluding Remarks

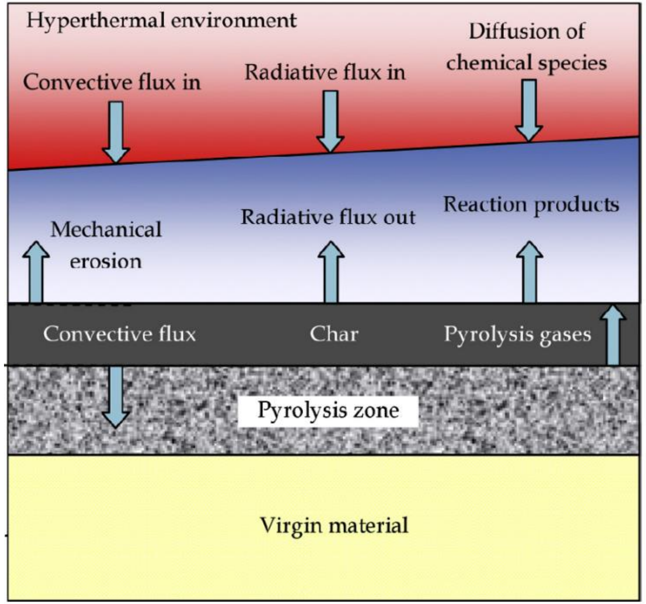
- UHTR-F neat resin has the highest char yield, highest Td, and residual masses increases with heating rates (an unusual behavior)
- Thermal stability was studied using 5, 10, 20, and 40^{o}C/min from 163^{o}C to 1000^{o}C in N_2
- dTGA was used to identify different reactions occur in the resin systems
- Isoconversion Code was used to calculate the kinetic parameters
- Different silica/UHTR composites were fabricated, tested, & evaluated

Study Case 2: Experimental Characterization of Material Properties of Novel Silica/Polysiloxane Ablative*

*K.J. Schellhase, J.H. Koo, H. Wu, J.J. Buffy, *J. of Spacecraft and Rockets*, (2018), doi: 10,2514/1.A34044; Funded by Techneglas.

Background: Ablatives

- Resists thermochemical erosion
- Char formation
- Pyrolysis zone
- Oxygen attack
  - Thermal stability increased in absence of oxygen
- Backside temperature



Phenomena in degrading ablatives

Background: SC-1008 Phenolic

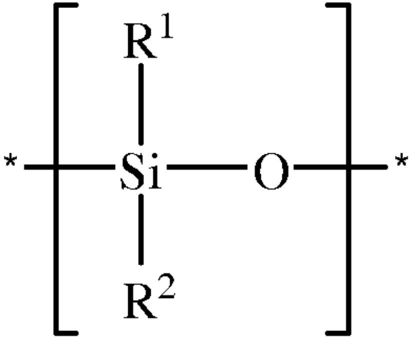
- MIL-standard phenolic resole resin manufactured by Hexion
- Typically carbon or silica fiber reinforcement
- Foamed versions of phenolic used for low density ablators
- Extensive data base
- Diverse applications, from TPS materials to rocket motor ablative materials
- Relatively inexpensive

Silica/Phenolic composite

Background: UHTR Polysiloxane

- Inorganic matrix, utilizing a mixture of polysiloxane chemistries patented and manufactured by Techneglas LLC, Perrysburg, OH (techneglas.com)
- Pre-ceramic material & high char yield
- Low heat release rate and heat release capacity
- Good compatibility with silica fabric

Silica/UHTR composite



Siloxane

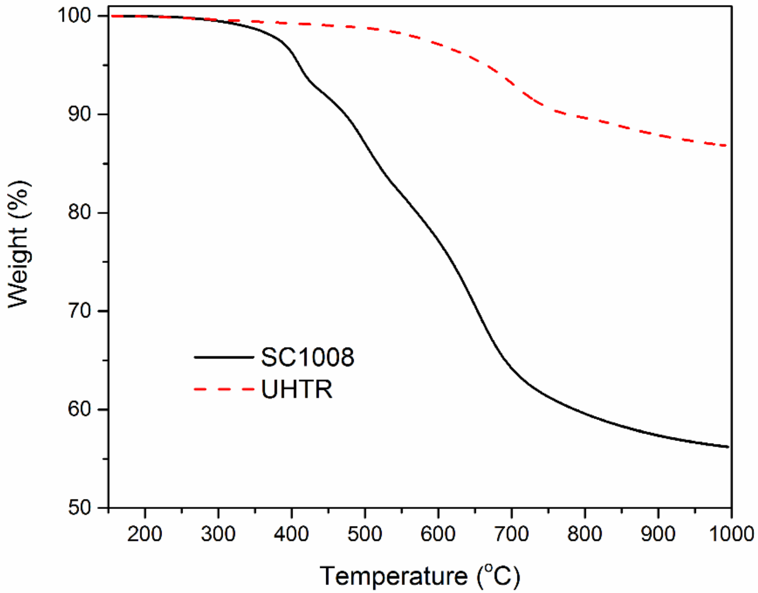
Research Objective

- Compare the thermal and ablative properties of the new UHTR resin to a legacy ablative resin (phenolic)
- Create a preliminary curing cycle for the UHTR, and use it to manufacture fiber reinforced polymers (FRPs)
- Evaluate the optimal Resin: Fiber ratio for the FRPs
- Better understand the UHTR's protective mechanism

Material Characterization

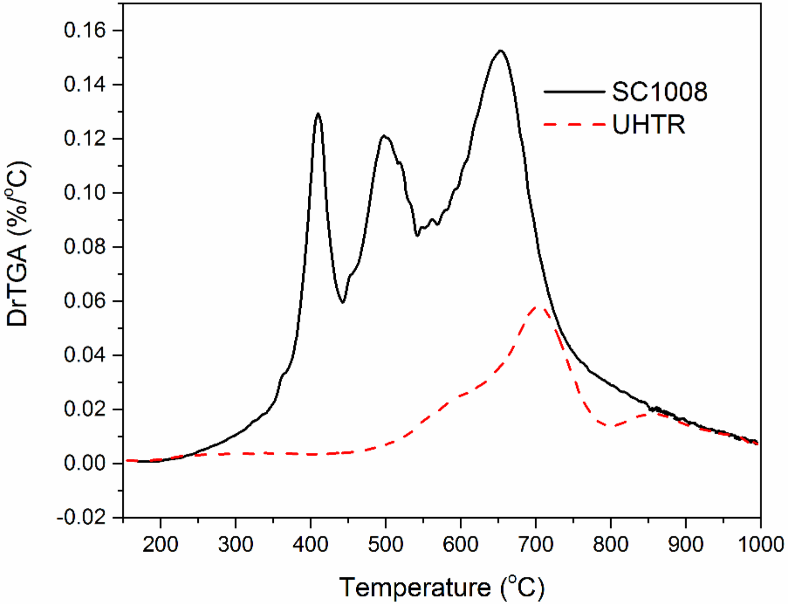
- Thermogravimetric analysis (TGA)
  - Thermal stability & char yield
- Microscale combustion calorimeter (MCC)
  - Heat release rate and capacity
- Density
  - Water displacement
- Oxy-acetylene test bed (OTB)
  - Ablative performance
  - Insulative property

Char Yield Study: 1



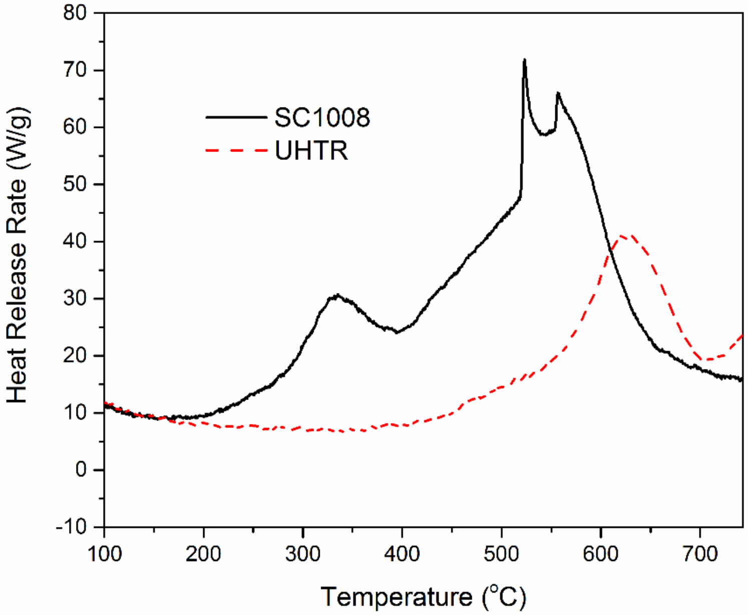
Char yield results for the neat SC-1008 and UHTR resins

Char Yield Study: 2



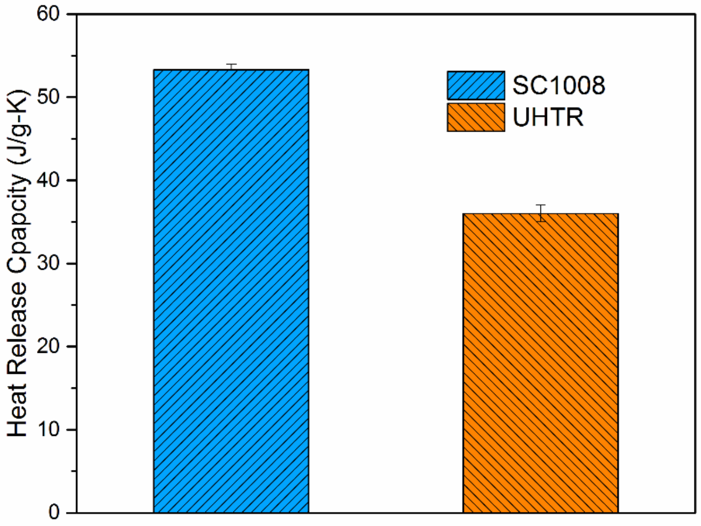
dTGA for the neat SC-1008 and UHTR resins

Flammability Properties: 1



Heat release rates for the two resin systems

Flammability Properties: 2

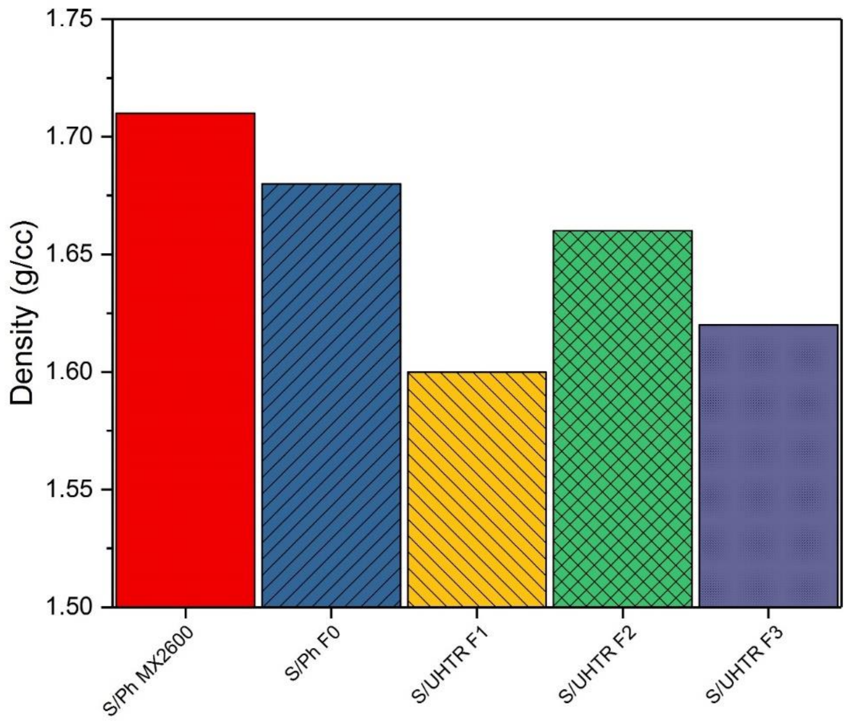


MCC heat release capacities for the two resin systems

Composite Test Samples

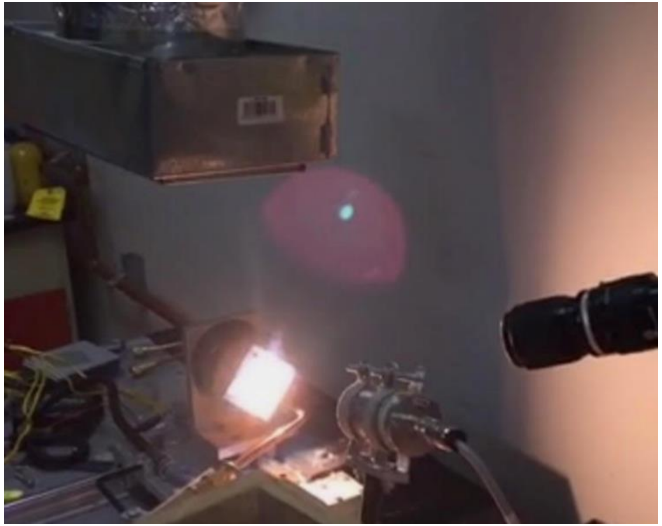
Sample ID	Resin %	Fiber %	Silica filler %
S/Ph MX2600	30-35% (burn-off)	64%	4.5%
S/Ph F0	39%	61%	0%
S/UHTR F1	35%	65%	0%
S/UHTR F2	40%	60%	0%
S/UHTR F3	48%	52%	0%

Density


1.75
1.70
1.65
1.60
1.55
1.50
Density (g/cc)
S/Ph MX2600
S/Ph F0
S/UHTR F1
S/UHTR F2
S/UHTR F3

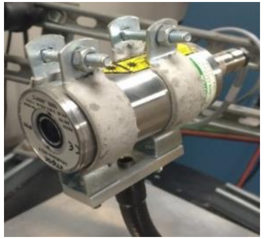
Oxy-Acetylene Test Bed

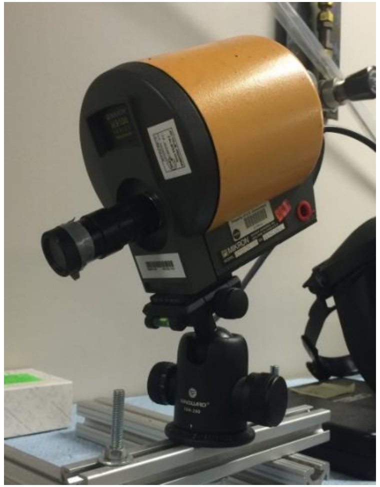
- Utilized a #4 welding torchy tip and high flow rates to create high heat fluxes
- Utilized a 1.1:1 Oxygen: Fuel ratio at 9.8:9 SLPM
- Tested at a heat flux of 1,000 W/cm^2, verified using Gardon heat flux gauge
- 40s exposure time
- Carbon-carbon shield



Experimental Setup

- Test Equipment
  - Two-color IR pyrometer
  - IR video camera
  - HD video camera
  - K-type thermocouple

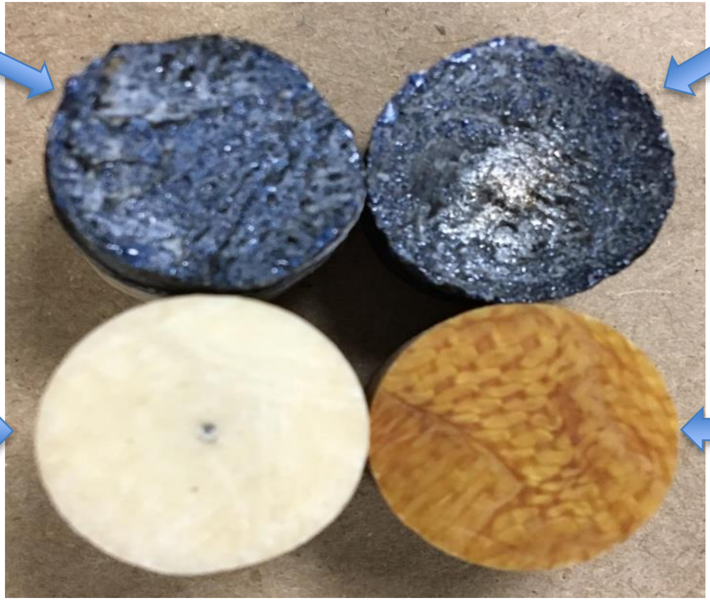




Ablation Testing

S/UHTR
Post-test

S/Ph
Post-test

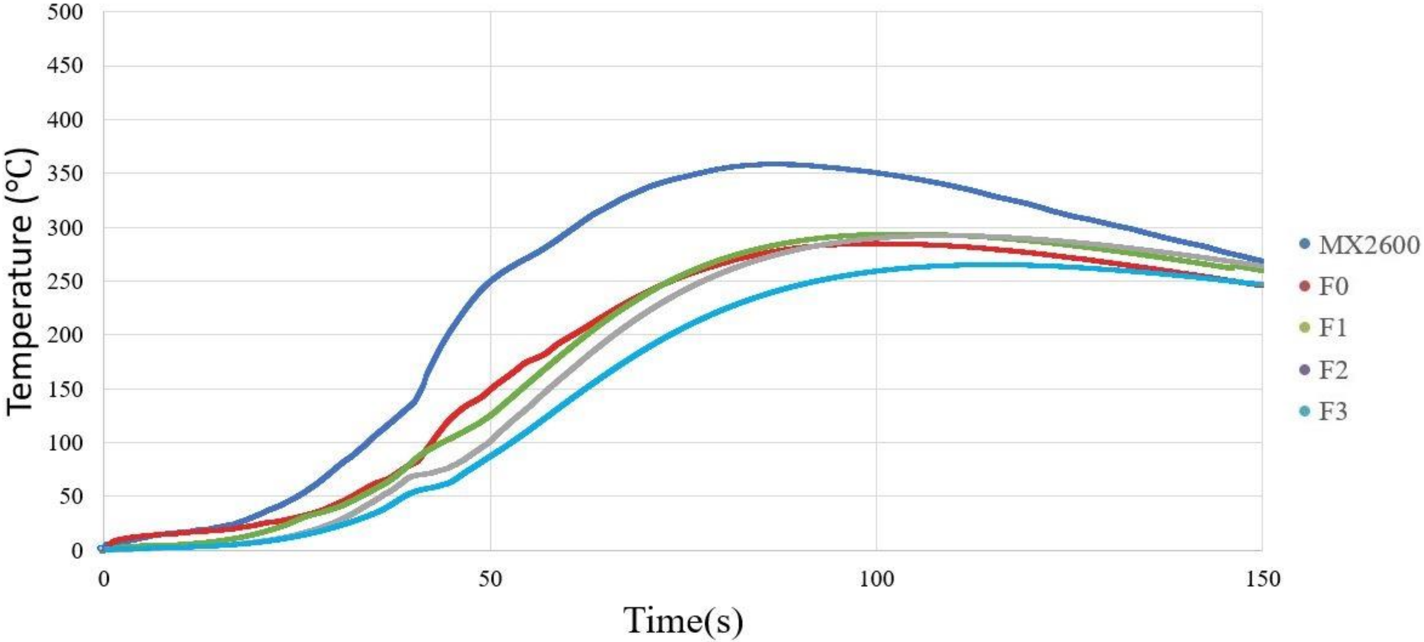


S/UHTR
Pre-test

S/Ph
pre-test

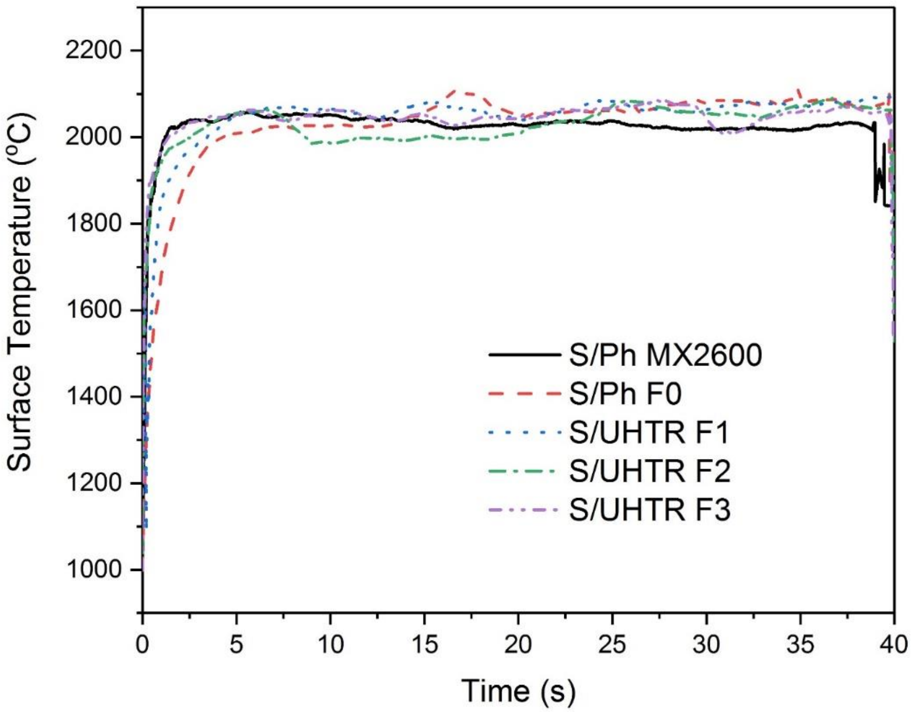
15mm diameter x 15mm thick samples

Backside Thermocouple Data

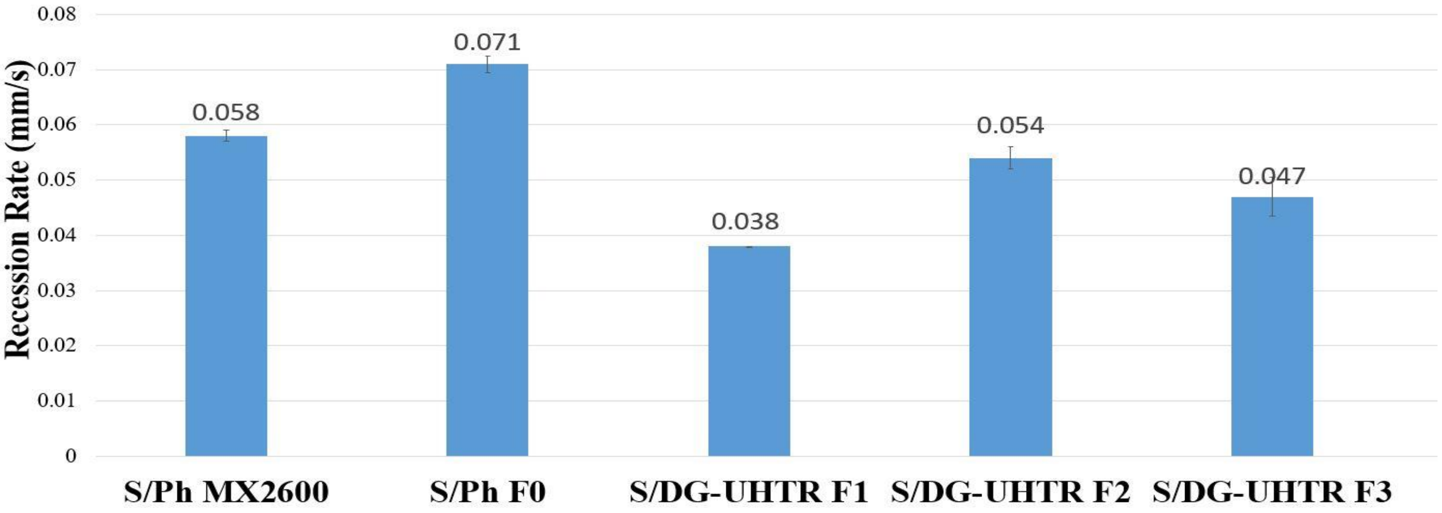


Temp vs. Time curves averaged from 6 Tests

Surface Temperature Data

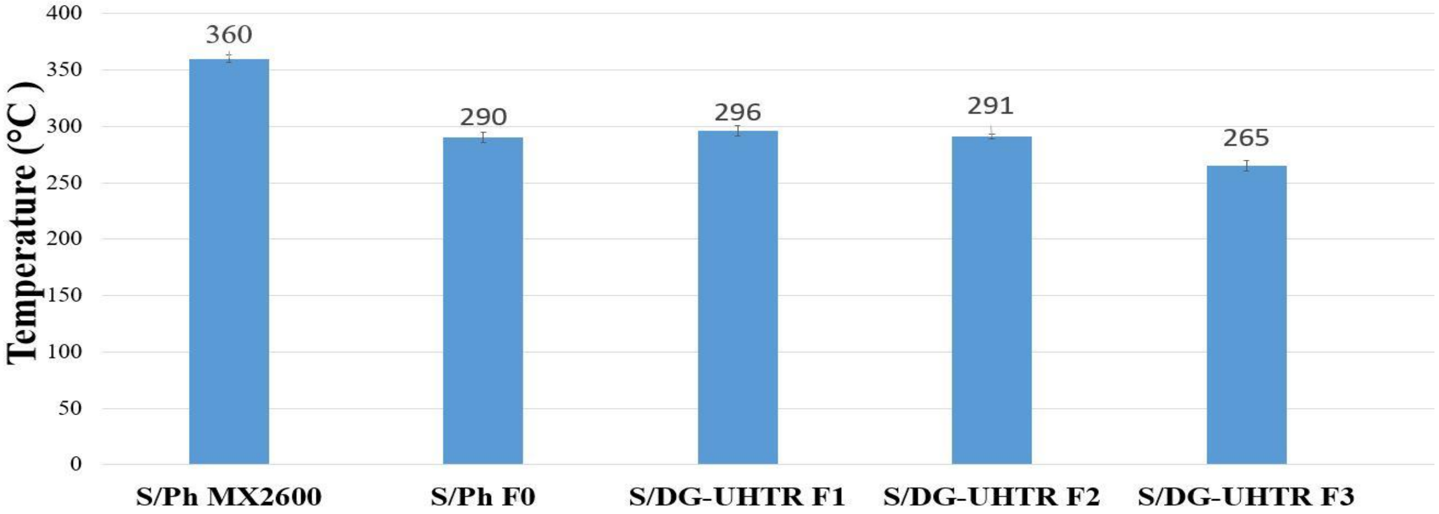


Recession Rate



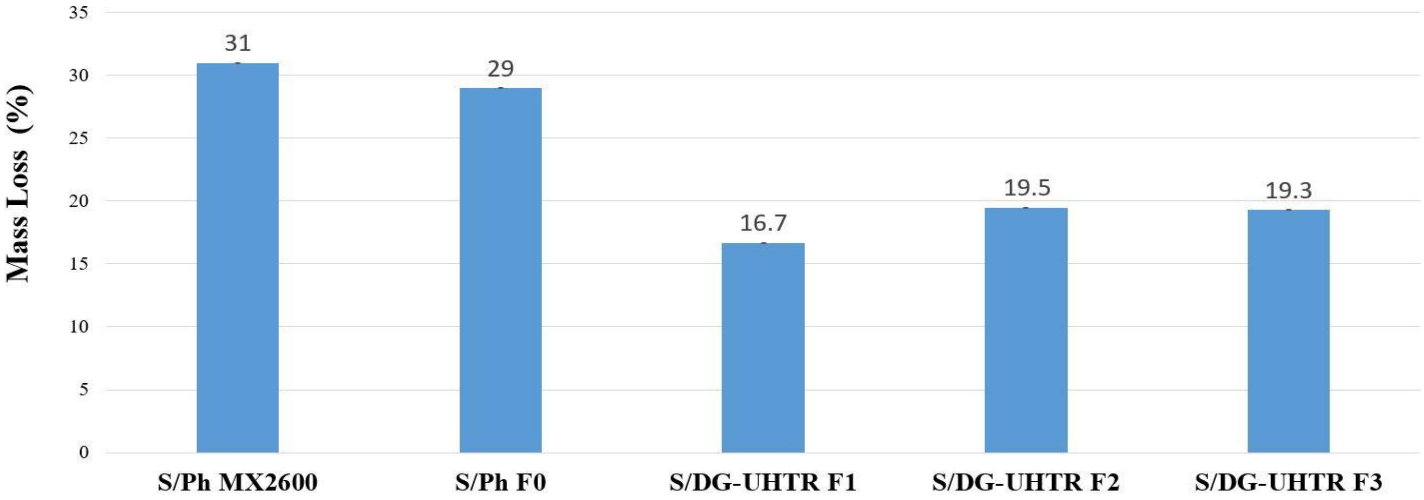
Resin: 30-35wt% 39wt% 35wt% 40wt% 48wt%

Heat-Soaked Temperature



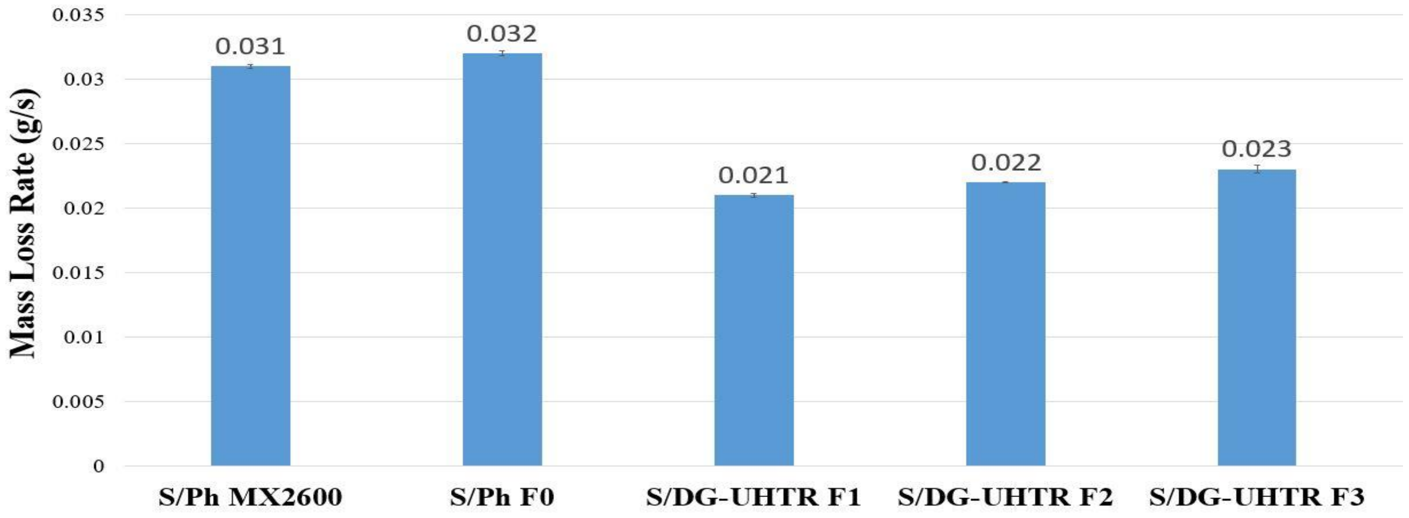
Resin: 30-35wt% 39wt% 35wt% 40wt% 48wt%

Mass Loss Percent



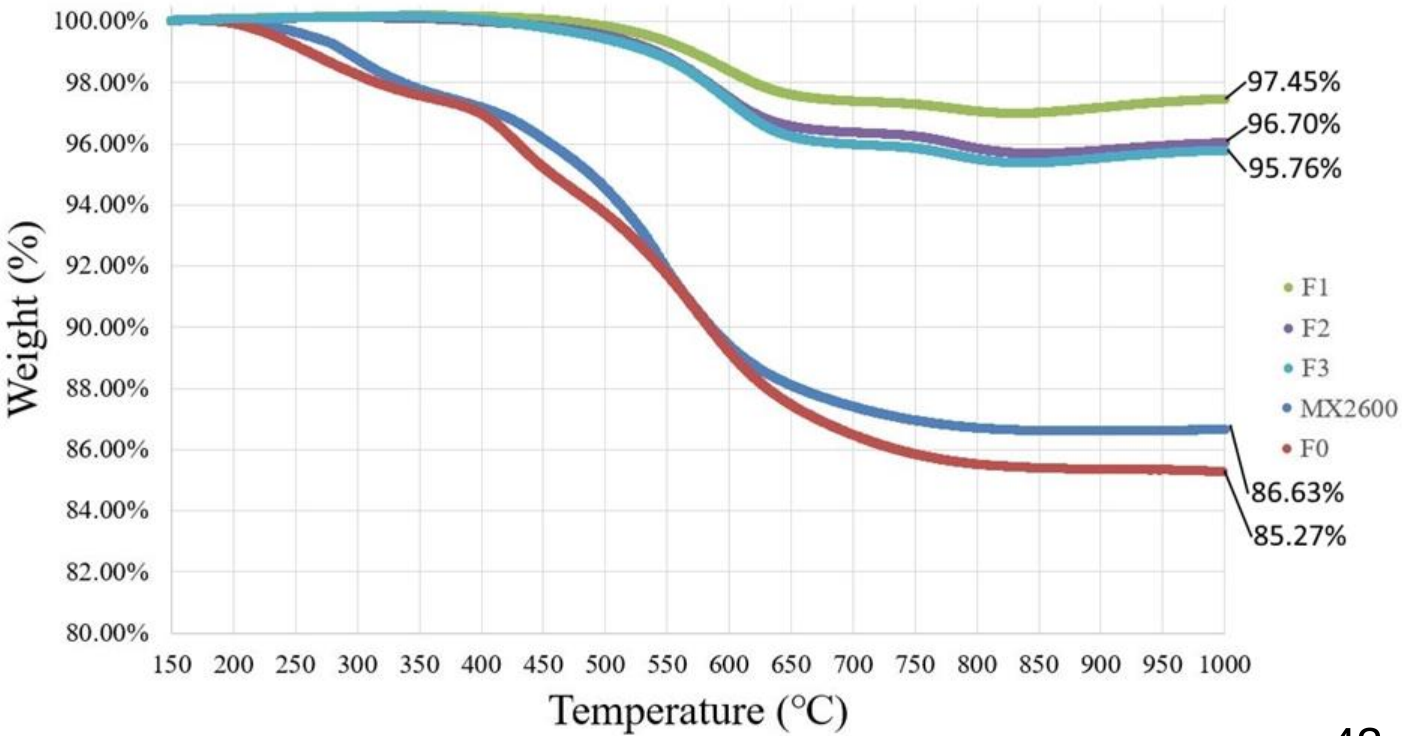
Resin: 30-35wt% 39wt% 35wt% 40wt% 48wt%

Mass Loss Rate

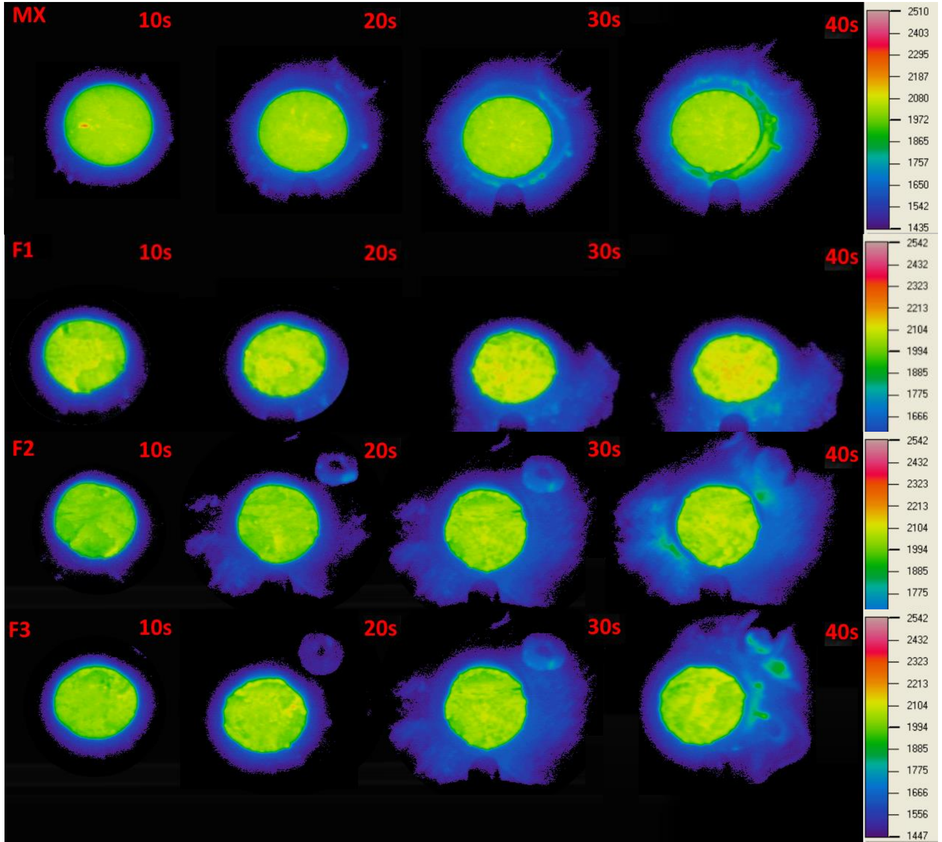


Resin:	**30-35wt%**	**39wt%**	**35wt%**	**40wt%**	**48wt%**

TGA


100.00%
98.00%
96.00%
94.00%
92.00%
90.00%
88.00%
86.00%
84.00%
82.00%
80.00%
Weight (%)
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
Temperature (°C)
97.45%
96.70%
95.76%
86.63%
85.27%
F1
F2
F3
MX2600
F0

IR Video


MX
10s
20s
30s
40s
F1
10s
20s
30s
40s
F2
10s
20s
30s
40s
F3
10s
20s
30s
40s
2510
2403
2295
2187
2080
1972
1865
1757
1650
1542
1435
2542
2432
2323
2213
2104
1994
1885
1775
1666
2542
2432
2323
2213
2104
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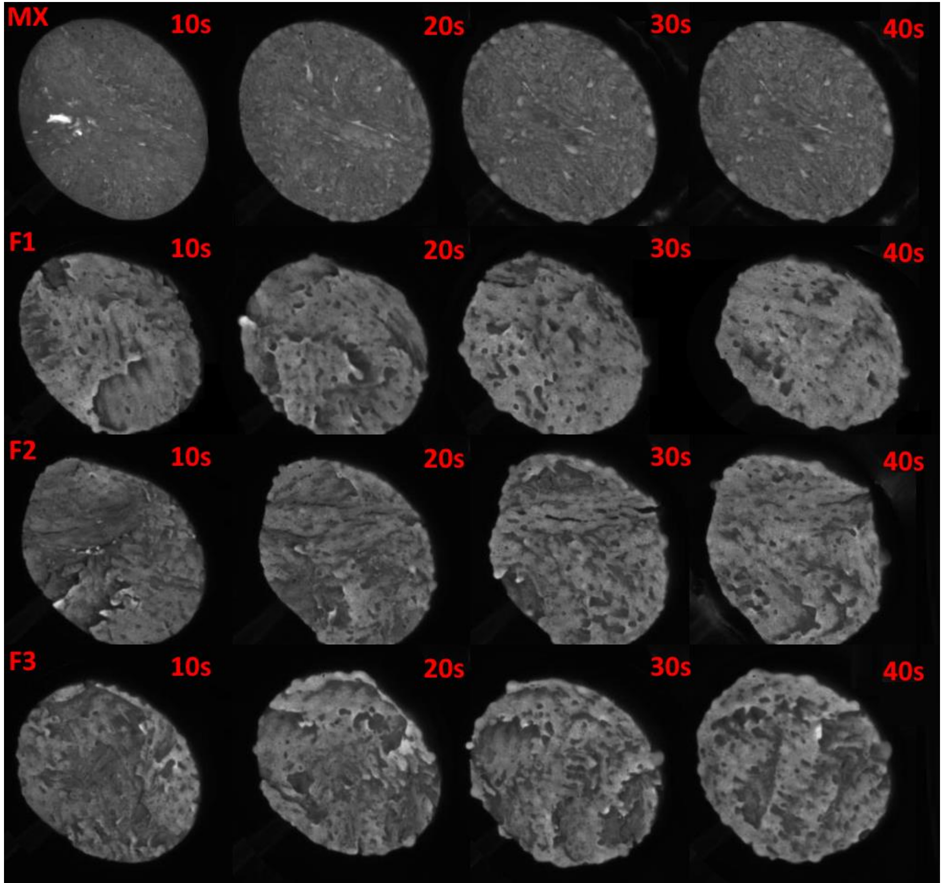
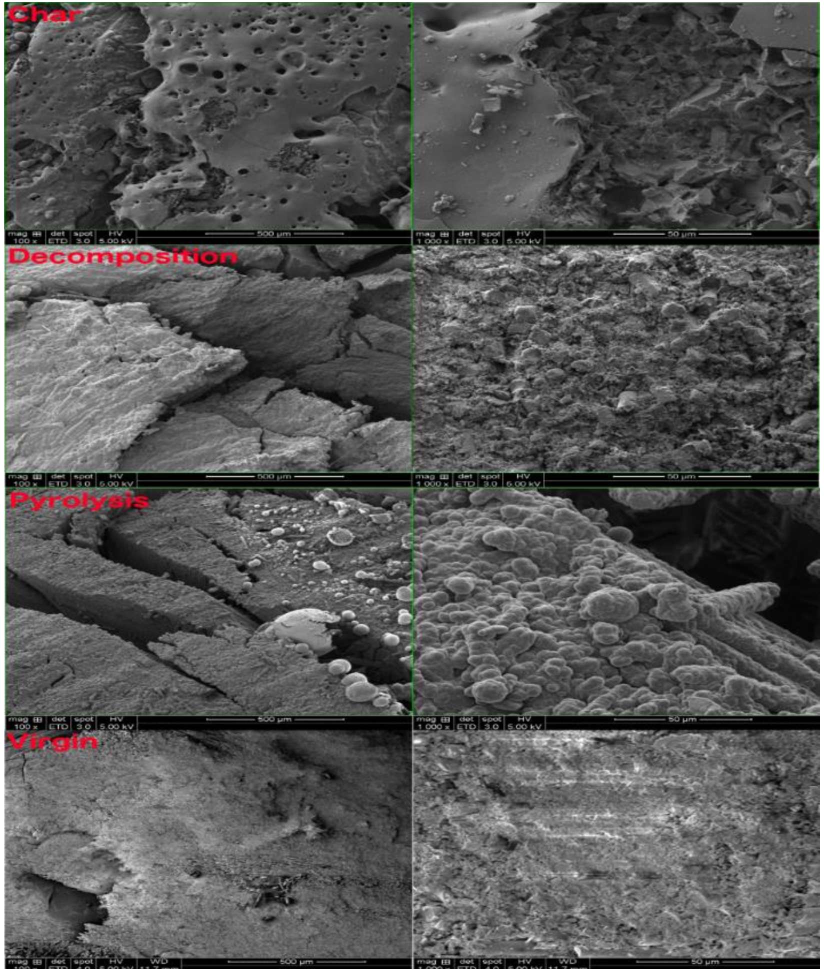
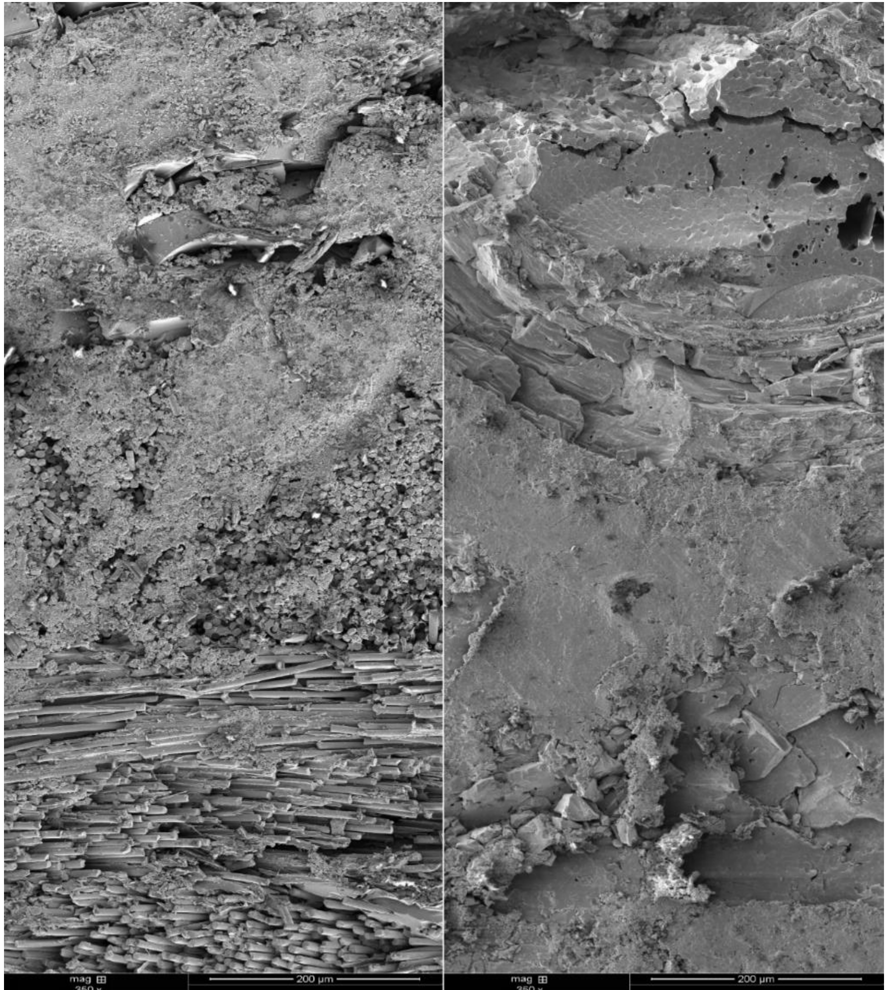
2323
2213
2104
1994
1885
1775
1666
1556
1447

HD Video


MX
10s
20s
30s
40s
F1
10s
20s
30s
40s
F2
10s
20s
30s
40s
F3
10s
20s
30s
40s



SEM micrographs of S/UHTR F2 showing (a) char zone (top view), (b) decomposition zone (side view), (c) pyrolysis zone (side view), and (d) virgin zone (side view) at 100x (left) and 1,000x (right) magnifications.



Cross-sectional-view SEM micrographs from char zone at the top of the sample for (a) S/Ph F0 (left) and (b) S/UHTR F2 (right) at 350x magnification.

Conclusions

- Silica/UHTR formulations showed the best ablation performance and insulative property.

- The 35 wt% Silica/UHTR F1 composite showed the highest char yield, lowest recession rate, and mass loss.

- The 48 wt% Silica/UHTR F3 composite showed the lowest peak heat-soaked temperature.

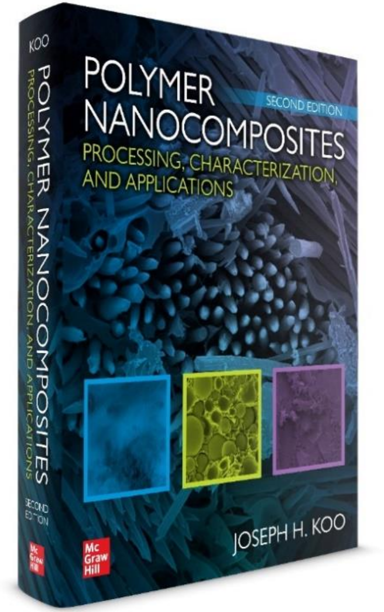
- Achieve better insulative and ablation performance with lower density than S/Ph composite.
    - Significant weight saving for composite structure
    - Less fuel to launch, dedicate more weight to cargo

Ongoing Research Projects

- To develop a dual layer concepts using UHTR-*n*-sialic/carbon fiber in MC format for top Recession Layer (RL) and a bottom Insulating Layer (IL) of UHTR-*n*-silica/glass mat.
- To develop an IL of UHTR with 3 types of aerogels for better insulating properties. Glass fibers will be adding to enhance mechanical properties.
- To develop a UHTR resin systems with catalyst for fast curing aims for additive manufacturing applications.
- To develop UHTR carbon fiber-reinforced composite using FW for hypersonic applications with Army Futures Command (AFC) through Army Research Lab (ARL).
- To develop a surface treatment for carbon fibers that will be compatible with a modified UHTR resin system to enhance interfacial bonding with Prof Bateman of RMIT University, Melbourne, Australia.
- To develop a low-density ablator using UHTR/FiberForm.

Polymer Nanocomposites: Processing, Characterization, and Applications, Second Edition, 2019

Up-to-date polymer nanocomposite principles, practices, and characteristics



This fully updated guide helps engineers and scientists understand and use the special properties of cutting-edge polymer nanocomposites.

Each chapter examines a different property (structural, mechanical, thermal, flammability, ablation, and electrical) and explains relevant commercial and industrial applications. Examples for a wide variety of usage include applications for spacecraft and defense vehicles, medical and dental implants, flame-retardant and conductive polymers for additive manufacturing, and fire-resistant woven and nonwoven fabrics.

Coverage includes:

- Nanotechnology and nanomaterials fundamentals
- Applications in an expansive range of industries and commercial sectors
- Processing of multifunctional polymer nanocomposites
- Structure and properties characterization
- Mechanical, thermal, flammability, ablation, electrical, and tribological properties
- Opportunities, trends, and challenges in the field